

**THERMALLY STABLE PERFLUOROPOLYETHERS AND PROCESSES
THEREFOR AND THEREWITH**

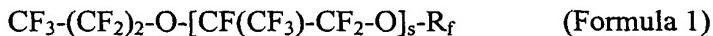
FIELD OF THE INVENTION

5 The invention relates to a fluorinated hydrocarbon having improved thermostability over the presently available fluorinated hydrocarbons, to a process therefor, and to a process therewith.

BACKGROUND OF THE INVENTION

10 Perfluoropolyethers (hereinafter PFPE) are fluids having important uses in oils and greases for use under extreme conditions. A property shared by the class is extreme temperature stability in the presence of oxygen and they find use in tribological or lubrication applications. Among their advantages as extreme lubricants is the absence of gums and tars among the thermal decomposition products. In contrast to the gum and tar thermal degradation products of hydrocarbons, the degradation products of PFPE fluids are volatile. In actual use, the upper temperature limit is determined by the stability of the oil or grease. Lewis acids, metal fluorides such as aluminum trifluoride or iron trifluoride, are formed as a result of heat at microscale loci of metal to metal friction; for instance as stationary bearings are started in motion. Thus the PFPE stability in the presence of the metal fluoride, although lower than the stability in the absence of the metal fluoride, establishes the upper performance temperature. The three commercial PFPEs, KRYTOX® (from E.I. du point de Nemours & Co., Inc., Wilmington DE), FOMBLIN® and GALDEN® (from Ausimont/Montedison, Milan, Italy) and DEMNUM® (from Daikin Industries, Osaka, Japan) differ in chemical structure. A review of KRYTOX® is found in *Synthetic Lubricants and High-Performance Fluids*, Rudnick and Shubkin, Eds. Marcel Dekker, New York, NY, 1999 (Chapter 8, pp. 215 – 237). A review of FOMBLIN® and GALDEN® is found in *Organofluorine Chemistry*, Banks, et al., Plenum, New York, NY, 1994, Chapter 20, pp. 431 – 461, and for DEMNUM, in *Organofluorine Chemistry (op. cit.)*, Chapter 21, pp. 463 – 467.

The anionic polymerization of hexafluoropropylene epoxide as described by Moore in US Patent 3,332,826 can be used to produce the KRYTOX® fluids. The resulting poly(hexafluoropropylene epoxide) PFPE fluids are hereinafter described as poly(HFPO) fluids. The initial polymer has a terminal acid fluoride, which is 5 hydrolyzed to the acid followed by fluorination. The poly(HFPO) fluid is shown by Formula 1:



where s is 2 - 100 and R_f is a mixture of CF₂CF₃ and CF(CF₃)₂, with the ratio of ethyl to isopropyl terminal group ranging between 20:1 to 50:1.

10 DEMNUM® fluids are produced by sequential oligomerization and fluorination of 2,2,3,3-tetrafluorooxetane, yielding the structure of Formula 2.

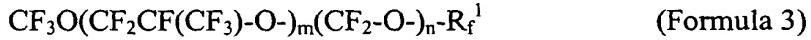


where R_f² is a mixture of CF₃ or C₂F₅ and t is 2 - 200.

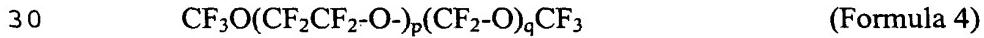
15 A common characteristic of the PFPE fluids is the presence of perfluoroalkyl terminal groups.

The mechanism of thermal degradation in the presence of a Lewis acid such as aluminum trifluoride has been studied. Kasai (Macromolecules, 25, 6791-6799, 1992) discloses an intramolecular disproportionation mechanism for the decomposition of PFPE containing -O-CF₂-O- linkages in the presence of Lewis acids. 20

FOMBLIN® and GALDEN® fluids are produced by perfluoroolefin photooxidation. The initial product contains peroxide linkages and reactive terminal groups such as fluoroformate and acid fluoride. These linkages and end groups are removed by ultraviolet photolysis and terminal group fluorination, to yield the 25 neutral PFPE compositions FOMBLIN® Y and FOMBLIN® Z represented by Formulae 3 and 4, respectively



where R_f¹ is a mixture of -CF₃, -C₂F₅, and -C₃F₇; (m + n) is 8 - 45; and m/n is 20 - 1000; and



where ($p + q$) is 40 - 180 and p/q is 0.5 - 2 . It is readily seen that Formulae 3 and 4 both contain the destabilizing -O-CF₂-O- linkage since neither n nor q can be zero. With this -O-CF₂-O- linkage in the chain, degradation within the chain can occur, resulting in chain fragmentation.

5 For PFPE molecules with repeating pendant -CF₃ groups, Kasai discloses the pendant group provides a stabilizing effect on the chain itself and for the alkoxy end groups adjacent to a -CF(CF₃)-. Absent the -O-CF₂-O- linkage, the PFPE is more thermally stable, but its eventual decomposition was postulated to occur at end away from the stabilizing -CF(CF₃)- group, effectively unzipping the polymer chain one ether unit at a time.

10 Therefore, there is substantial interest and need in increasing the thermal stability of PFPE fluids.

SUMMARY OF THE INVENTION

15 According to a first embodiment of the invention, a perfluoropolyether is provided, which comprises perfluoroalkyl radical end groups in which the perfluoroalkyl radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl end groups, and 1,2-bis(perfluoromethyl)ethylene diradicals [-CF(CF₃)CF(CF₃)-] are absent in the molecule.

20 According to a second embodiment of the invention, a process for improving the thermal stability of a perfluoropolyether is provided, which comprises modifying a process for producing a perfluoropolyether such that substantially or essentially all end groups of the perfluoropolyether have at least 3 carbon atoms per end group or, preferably, are C₃-C₆ branched and straight chain perfluoroalkyl end groups.

25 According to a third embodiment of the invention, a process is provided for producing a perfluoropolyether comprising perfluoroalkyl radical end groups in which the perfluoroalkyl radical has at least 3 carbon atoms per radical as disclosed in the first embodiment of the invention. The process can comprise (1) contacting a perfluoro acid halide, a C₂ to C₄-substituted ethyl epoxide, a C₃⁺ fluoroketone, or
30 combinations of two or more thereof with a metal halide to produce an alkoxide; (2)

contacting the alkoxide with either hexafluoropropylene or tetrafluorooxetane to produce a second acid halide; (3) esterifying the second acid halide to an ester; (4) reducing the ester to its corresponding alcohol; (5) converting the corresponding alcohol with a base to a salt form; (6) contacting the salt form with a C₃ or higher olefin to produce a prepolyether; and (7) fluorinating the prepolyether.

5 According to a fourth embodiment of the invention, a thermally stable grease or lubricant is provided, which comprises a thickener with a perfluoropolyether composition disclosed in the first embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

10 This invention is directed to a thermal stable perfluoropolyether (or PFPE) composition and processes for making and using the composition. The term "perfluoropolyether" and "PFPE fluid" ("PFPE" or "PFPE fluids") are, unless otherwise indicated, exchangeable.

According to the first embodiment of the invention, there is provided a
 15 perfluoropolyether comprising branched or straight chain perfluoroalkyl radical end groups, each of which has at least 3 carbon atoms per radical, is substantially or essentially free of perfluoromethyl and perfluoroethyl end groups and does not contain any 1,2-bis(perfluoromethyl)ethylene diradicals [-F(CF₃)CF(CF₃)-] in the chain. The term "substantially", as used herein, refers to a perfluoropolyether or
 20 PFPE fluid of this invention having only trace C₁-C₂ perfluoroalkyl endgroups such that the initial decomposition in a specific use is inconsequential and tolerable. An unavoidable trace of remaining perfluoropolyether or PFPE molecules with a perfluoro-methyl or -ethyl end group, while not desirable, may be tolerable as such molecules degrade to volatile products, leaving the more stable PFPE molecules.
 25 Thus thermal stability increases after some initial degradation.

The preferred perfluoropolyethers have the formula of C_rF_(2r+1)-A-C_rF_(2r+1) in which each r is independently 3 to 6; if r = 3, both end groups C_rF_(2r+1) are perfluoro-n-propyl radicals; A can be O-(CF(CF₃)CF₂-O)_w, O-(CF₂-O)_x(CF₂CF₂-O)_y, O-(C₂F₄-O)_w, O-(C₂F₄-O)_x(C₃F₆-O)_y, O-(CF(CF₃)CF₂-O)_x(CF₂-O)_y, O-(CF₂CF₂CF₂-O)_w, O-(CF(CF₃)CF₂-O)_x(CF₂CF₂-O)_y-(CF₂-O)_z, or combinations of two or more

thereof; preferably A is O-(CF(CF₃)CF₂-O)_w, O-(C₂F₄-O)_w, O-(C₂F₄-O)_x(C₃F₆-O)_y, O-(CF₂CF₂CF₂-O)_w, or combinations of two or more thereof; w is 4 to 100; x and y are each independently 1 to 100.

Such compositions, as illustrated in the EXAMPLES section, show a
5 significant increase in thermal stability over the corresponding PFPE fluids having perfluoroethyl or perfluoromethyl end groups. Similarly, stability of those PFPE fluids subject to degradation at the perfluoroalkyl terminal group, in addition to those based on poly(HFPO), can be improved by replacing the less stable -CF₃ and -C₂F₅ groups with, for example, C₃-C₆ perfluoroalkyl groups.

10 According to the second embodiment of the invention, a process for improving the thermal stability of a perfluoropolyether is provided. The process can comprise (1) incorporating one C₃⁺ terminal segment is formed into a perfluoropolyether precursor to produce a precursor having an initial C₃⁺ end group; (2) polymerizing the precursor having an initial C₃⁺ end group to a desired molecular weight polymer containing an alkoxide growing chain; (3) incorporating a second C₃⁺ end group to produce a polyether having both C₃⁺ end groups; and (4) fluorinating the polyether having both C₃⁺ end groups. The term "C₃⁺" refers to 3 or more carbon atoms.
15

Several processes are available for producing a PFPE fluid having improved
20 thermal stability. The process is more fully disclosed in the third embodiment of the invention, which is provided only as examples, other similar processes are evident to those skilled in the art. For example purposes, poly(HFPO) fluids may be subjected to exacting fractional distillation under vacuum. In practice, the upper molecular weight limit for such a distillation is the separation and isolation of F(CF(CF₃)-CF₂-O)₉-CF₂CF₃ and F(CF(CF₃)-CF₂-O)₉-CF(CF₃)₂. The increased thermal stability
25 isopropyl over ethyl, described in the EXAMPLES, demonstrates the present invention.

The invention disclosed below discloses perfluoropolyether having preferred C₃-C₆ perfluoroalkyl end groups. It is, however, within the scope of the invention
30 that the disclosure is also applicable to any C₃⁺ perfluoroalkyl end group. In the case

of KRYTOX®, for instance, the resultant poly(HFPO) chain terminates at both ends with C₃-C₆ perfluoroalkyl groups, having the formula of C_rF_(2r+1)-O-[-CF(CF₃)-CF₂-O-]_s-C_rF_(2r+1) (**Formula 5**) where s is 2-100 and r is 3-6.

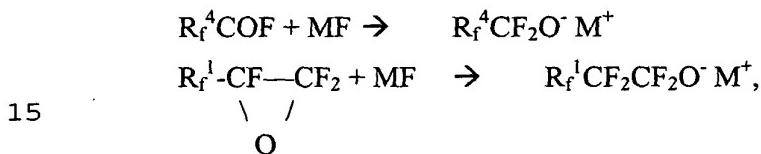
According to the third embodiment of the invention, a process for producing
 5 a perfluoropolyether in which substantially all perfluoroalkyl end groups of the perfluoropolyether contain at least three, preferably 3 to 6, carbon atoms per end group. The perfluoropolyether has the formula of C_rF_(2r+1)-A-C_rF_(2r+1) as disclosed in the first embodiment of the invention. The process can comprise (1) contacting a perfluoro acid halide, a C₂ to C₄-substituted ethyl epoxide, a C₃⁺ fluoroketone, or
 10 combinations of two or more thereof with a metal halide to produce an alkoxide; (2) contacting the alkoxide with either hexafluoropropylene or tetrafluorooxetane to produce a second acid fluoride; (3) contacting the second acid fluoride with an alcohol to produce an ester; (4) reducing the ester to corresponding alcohol; (5) contacting the corresponding alcohol with a base to a salt form; (6) contacting the
 15 salt form with a C₃⁺ or higher olefin to produce a prepolyether; and (7) Fluorinating the prepolyether to produce the perfluoropolyether of the invention.

Typically, one C₃⁺ terminal segment is produced first (the “initial end group”) followed by its polymerization using, for example, hexafluoropropylene oxide or tetrafluorooxetane to a desired molecular weight polymer. This polymer is
 20 thermally treated to convert the growing alkoxide chain to an acid fluoride. The acid fluoride is converted to an ester, which is then reduced to its corresponding alcohol. The second C₃⁺ terminal group (the “final end group”) is now incorporated into the polymer by, for example, treatment with a mineral base in a suitable solvent and the addition of a reactive hydro- or fluoro-olefin. Reactive hydroolefins include allyl
 25 halides and tosylates. Finally the PFPE is formed by replacing substantially or essentially all hydrogen atoms with fluorine atoms.

Process 1 discloses a process for producing PFPEs terminated with paired normal C₃ to C₆ end groups. The process comprises (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with a metal halide to produce an
 30 alkoxide; (2) contacting the alkoxide with either hexafluoropropylene or

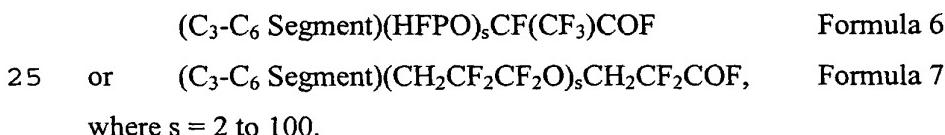
tetrafluorooxentane to produce a second acid halide; (3) contacting the second acid halide with an alcohol to produce an ester; (4) reducing the ester to corresponding alcohol; (5) contacting the corresponding alcohol with a base to a salt form; (6) contacting the salt form with a C₃ or higher olefin to produce a prepolyether; and (7) 5 fluorinating the prepolyether to produce the perfluoropolyether of the invention. The preferred halide, unless otherwise indicated, is fluoride and the preferred base is a metal hydroxide such as, for example, alkali metal hydroxide as used below to illustrate these steps.

Step 1 involves the contact of either a C₃-C₆ perfluoro acid fluoride or a C₂ to 10 C₄ substituted ethyl epoxide with a metal fluoride, such as CsF or KF, in a suitable solvent such as tetraethylene glycol dimethyl ether at temperatures from about 0° to about 100°C to form an alkoxide which can be further polymerized.



where preferred M is cesium or potassium, R_f⁴ is C_aF_(2a+1), a is 2 to 5, R_f¹ is C_bF_(2b+1), and b is 1 to 3.

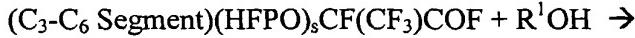
Step 2 involves the contact of the alkoxide with either hexafluoropropylene 20 oxide or tetrafluorooxetane at low temperature, about -30° to about 0°C, followed by thermolysis at >50°C, to produce the PFPE with one C₃-C₆ end group and an acid fluoride on the other terminus, and having the Formula 6 (from HFPO) or Formula 7 (from tetrafluorooxetane).



Alternatively, Formula 7 can be converted to an equivalently useful acid fluoride by replacing all methylene hydrogen radicals with fluorine radicals using the fluorination procedure disclosed in Step 7, with or without the use of a suitable 30 solvent, at temperatures of about 0° to about 180°C, and with autogenous or elevated fluorine pressures of 0 to 64 psig (101 to 543 kPa). The resulting perfluorinated acid fluoride is then further processed as follows.

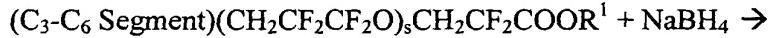


- Step 3 involves the contact of the acid fluoride with an alcohol such as methanol, with or without solvent or excess alcohol, at a temperature of about 0° to 5 about 100°C, producing the corresponding ester. HF produced can be removed by washing with water.

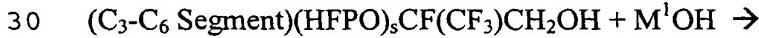


where s is 2 - 100 and R¹OH is an alcohol, preferably CH₃OH.

- In Step 4, the ester is reduced with a reducing agent such as, for example, sodium borohydride or lithium aluminum hydride in a solvent such as an alcohol or THF (tetrahydrofuran) at a range of temperatures (0° to 50°C) and at autogenous pressure for a time period of from about 30 minutes to about 25 hours to produce the corresponding alcohol (PFPE precursor):



- In Step 5, the PFPE precursor alcohol is converted to a metal salt. The conversion can be effected by contacting the precursor alcohol with a metal hydroxide, optionally in a solvent, under a condition sufficient to produce the metal salt. The presently preferred metal hydroxide includes alkali metal hydroxide and alkaline earth metal hydroxide, such as, for example, potassium hydroxide. Any solvent, such as, for example, acetonitrile, that does not interfere with the production of the metal salt can be used. Suitable condition includes a temperature in the range of from about 20° to about 100°C under a pressure of about 300 to about 1,000 mmHg (40 - 133 kPa) for about 30 minutes to about 25 hours.



- or (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OH + M¹OH →
 (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OM¹,
 or (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OH + M¹OH →
 (C-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OM¹,
- 5 (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OH + M¹OH →
 (C₃-C₆ Segment) - (CH₂CF₂CF₂O)_sCH₂CF₂CH₂OM¹,
 or (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OH + M¹OH →
 (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OM¹,
 or (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OH + M¹OH →
 10 (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OM¹,
 where M¹ is a metal such as alkali metal or alkaline earth metal and s is as defined above.

In Step 6, the metal salt is contacted with an olefin to produce a C₃ - C₆ segment prepolyether. The contacting can be carried out in the presence of a solvent such as, for example, an ether, under a condition to produce a prepolyether that can be converted to perfluoropolyether of the invention by fluorination disclosed herein below. Any olefin having more than three carbon atoms, preferably 3 to 6, can be used. The olefin can also be substituted with, for example, a halogen. Examples of such olefins include, but are not limited to, hexafluoropropylene, octafluorobutene, perfluorobutylethylene, perfluoroethylethylene, perfluorohexene, allyl halides, and combinations of two or more thereof. Additionally, a C₃ - C₆ segment containing a moiety known in the art to be a good leaving group in nucleophilic displacement reactions, for example a tosylates, can also be used. The contacting condition can include a temperature in the range of from about 0 to about 100°C under a pressure in the range of from about 0.5 to about 64 psig (105 - 543 kPa) for about 30 minutes to about 25 hours.

- (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OM¹ + R_f³CF=CF₂ →
 (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OCF₂CFHR_f³,
 where R_f³ is C_cF_(2c+1), and c is 2 to 4, and s is 2 to 100,
 30 or (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OM¹ + XCHR²CH=CH₂ →
 (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OCH₂CH₂CHR²,

- where R^2 is $C_bH_{(2b+1)}$, b is 1 to 3, and X is a halogen,
 or $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OM^1 + R_f^1CH=CH_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH_2R_f^1$,
 where R_f^1 is $C_bF_{(2b+1)}$ and b is 1 to 3.
- 5 $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OM^1 + R_f^3CF=CF_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCF_2CFH R_f^3$,
 where R_f^3 is $C_cF_{(2c+1)}$ and c is 2 to 4
 or $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OM^1 + XCHR^2CH=CH_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCH_2CH_2CHR^2$,
- 10 where R^2 is $C_bH_{(2b+1)}$, b is 1 to 3, and X is a halogen,
 or $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OM^1 + R_f^1CH=CH_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCH_2CH_2R_f^1$,
 where M^1 is an alkali metal or an alkaline earth metal and R_f^1 is $C_bF_{(2b+1)}$ and b is 1 to 3.
- 15 In Step 7, the perfluoropolyether with paired C3 to C6 segments is formed with elemental fluorine using techniques as described in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 11, page 492 (op. cit.) and references therein.
 $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCF_2CFHR_f^1 + F_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2R_f^1$,
 where R_f^1 is $C_bF_{(2b+1)}$ and b is 1 to 3,
 or $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH_2CHR^3 + F_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2CFR_f^5$,
 where R_f^5 is $C_dF_{(2d+1)}$, R^3 is $C_dH_{(2d+1)}$, and d is 0 to 3.
- 20 or $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CH_2OCH_2CH_2R_f^1 + F_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(HFPO)_sCF(CF_3)CF_2OCF_2CF_2CFR_f^1$,
 where R_f^1 is $C_bF_{(2b+1)}$, and b is 1 to 3,
 $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCF_2CFHR_f^1 + F_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ Segment})(CF_2CF_2CF_2O)_sCF_2CF_2CF_2OCF_2CF_2R_f^1$,
- 25 where R_f^1 is $C_bF_{(2b+1)}$ and b is 1 to 3
 or $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCH_2CH_2CHR^3 + F_2 \rightarrow$
- 30 where R_f^1 is $C_bF_{(2b+1)}$ and b is 1 to 3
 or $(C_3\text{-}C_6 \text{ Segment})(CH_2CF_2CF_2O)_sCH_2CF_2CH_2OCH_2CH_2CHR^3 + F_2 \rightarrow$

(C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCF₂CF₂CF₂OCF₂CF₂CHR_f⁵, where R³ is C_dH_(2d+1), d = 0 to 3, R_f⁵ is C_dF_(2d+1), and d is 0 to 3, or (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂CH₂OCH₂CH₂R_f¹ + F₂ → (C₃-C₆ Segment)(CF₂CF₂CF₂O)_sCF₂CF₂CF₂OCF₂CF₂R_f¹, 5 where R_f¹ is C_bF_(2b+1) and b is 1 to 3.

Process 2A discloses the synthesis of PFPEs terminated with a normal C₃ to C₆ initial end group and a branched C₃ to C₆ final end group. Steps 1 to 5 are the same as those in Process 1. The terminal fluoro alkene or allyl halide in Step 6 is replaced with either a branched fluoroalkene such as 2-perfluorobutene or a 10 branched allyl halide such as 1-bromo-3-butene. Step 7 is as described in Process 1. (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OH + M¹OH + R_f⁶CF=CFR_f⁷ → (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OCF(R_f⁶)CFHR_f⁷, where R_f⁶ is C_eF_(2e+1), R_f⁷ is C_fF_(2b+1), such that e and f ≥ 0, (e + f) ≤ 4 and (e + f) ≥ 1, or (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OH + M¹OH + XCR⁴CH=CHR⁵ 15 (C₃-C₆ Segment)(HFPO)_sCF(CF₃)CH₂OCH(R⁴)CH₂CHR⁵ where M¹ is the same as disclosed above, R⁴ is C_gH_(2g+1), R⁵ is C_hH_(2h+1), such that g and h ≥ 0 and (g + h) is 1 to 3.

Process 2B describes the synthesis of PFPEs terminated with a normal C₃ to C₆ initial end group and a branched C₃ to C₆ final end group. Steps 1 to 3 are followed from Process 1. The ester disclosed in step 3 is then contacted with a Grignard Reagent of the type C₂H₅M²X or CH₃M²X, where M² is magnesium or lithium, forming the carbinol which can either be dehydrated or fluorinated directly in Step 7 is as described in Process 1 to the desired PFPE. Steps 4 through 6 disclosed in Process 1 are omitted. 25 (C₃-C₆ Segment)(HFPO)_sCF(CF₃)C(O)OR¹ + 2 R⁶M²X → (C₃-C₆ Segment)(HFPO)_sCF(CF₃)C(OH)(R⁶)₂, (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂COOR¹ + 2R⁶M²X → (C₃-C₆ Segment)(CH₂CF₂CF₂O)_sCH₂CF₂C(OH)(R⁶)₂, where s is 2 – 100, R⁶ is CH₃ or C₂H₅ such that the total number of carbons in the 30 final segment is 3 to 6. (C₃-C₆ Segment)(CF₂CF₂CF₂O)_sCF₂CF₂COOR¹ + 2R⁶M²X →



where M² is magnesium or lithium, s is 2 - 100, R¹ is alkyl and preferably methyl, and R⁶ is CH₃ or C₂H₅ such that the total number of carbons in the final segment is 3 to 6.

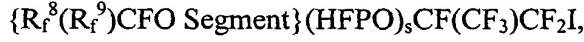
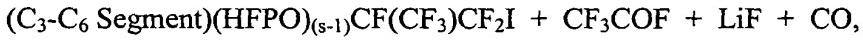
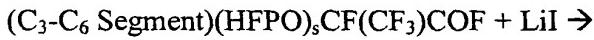
5 Process 3 discloses the synthesis of PFPEs terminated with a branched C₃ to C₆ initial end group and a normal C₃ to C₆ final end group. The reagents, either the acid fluoride or epoxide, in Step 1 of Process 1, are replaced with a C₃ to C₆ fluoroketone. Steps 2 to 7 of Process 1 are the same as Process 1.



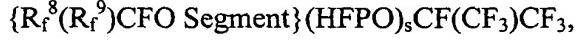
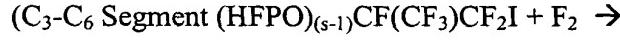
10 where R_f⁸ is C_jF_(2j+1), R_f⁹ is C_kF_(2k+1), such that j and k ≥ 0, (j + k) ≤ 3, and MF is a metal fluoride, such as CsF or KF.

Process 4 discloses the synthesis of PFPEs terminated with paired branched C₃ to C₆ end groups. Step 1 of Process 3 is practiced, followed by Steps 2 to 5 of Process 1, followed by Step 6 of Process 2A, and then finally Step 7 of Process 1.

15 Process 5A discloses an additional preferred procedure for making PFPEs with a C₃-C₆ initial end group with a branched C₃ final end group, which comprises (1) contacting a PFPE acid fluoride precursor prepared in Steps 1 and 2 of Process 1 or Steps 1 and 2 of Process 3 using hexafluoropropylene oxide with, for instance, lithium iodide at temperatures of at least 220°C to produce the corresponding iodide; and (2) fluorinating the corresponding iodide to produce the perfluoropolyether.



25 where R_f⁸ is C_jF_(2j+1), R_f⁹ is C_kF_(2k+1), such that j and k ≥ 0 and (j + k) ≤ 3,



30 where R_f⁸ is C_jF_(2j+1), R_f⁹ is C_kF_(2k+1), such that j and k ≥ 0 and (j + k) ≤ 3.

Process 5B is a modification of process 5A. The process comprises (1) contacting a PFPE acid fluoride precursor, produced as in Process 1 Step 1 or Process 3 Steps 1 and 2, using HFPO with an alkali metal halide, such as, for example lithium iodide, to produce the corresponding iodide; then (2) reducing the 5 iodine radical to a hydrogen radical using a suitable reducing agent such as sodium methylate at temperatures of 25° to 150°C and autogenous pressure, and (3) fluorinating the corresponding hydrogen radical to produce the PFPE.

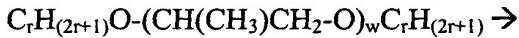
- Step 1: $(C_3\text{-}C_6 \text{ segment})(HFPO)_sCF(CF_3)\text{COF} + LiI \rightarrow$
 $(C_3\text{-}C_6 \text{ segment})(HFPO)_{(s-1)}CF(CF_3)CF_2I + CF_3\text{COF} + LiF + CO,$
- 10 or $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)\text{COF} + LiI \rightarrow$
 $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)CF_2I,$
where R_f^8 is $C_jF_{(2j+1)}$, R_f^9 is $C_kF_{(2k+1)}$, such that $(j+k) \leq 3$.
- Step 2: $(C_3\text{-}C_6 \text{ segment})(HFPO)_{(s-1)}CF(CF_3)CF_2I + NaOCH_3/HOCH_3 \rightarrow$
 $(C_3\text{-}C_6 \text{ segment})(HFPO)_{(s-1)}CF(CF_3)CF_2H,$
- 15 or $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)\text{COF} + NaOCH_3/HOCH_3 \rightarrow$
 $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)CF_2H,$
where R_f^8 is $C_jF_{(2j+1)}$, R_f^9 is $C_kF_{(2k+1)}$, such that $j \geq 0$ and $(j+k) \leq 3$.
- Step 3: $(C_3\text{-}C_6 \text{ segment})(HFPO)_{(s-1)}CF(CF_3)CF_2H + F_2 \rightarrow$
 $(C_3\text{-}C_6 \text{ segment})(HFPO)_{(s-1)}CF(CF_3)CF_3,$
- 20 or $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)CF_2H + F_2 \rightarrow$
 $\{R_f^8(R_f^9)\text{CO segment}\}(HFPO)_sCF(CF_3)CF_3.$

Process 6 discloses the synthesis of PFPEs terminated with $C_3\text{-}C_6$ end groups by the fluorination of corresponding hydrocarbon polyethers, following the process described in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, 25 Vol. 11, pages 492 (op. cit.) and specifically as described by Bierschenk et al. in US Patents 4,827,042, 4,760,198, 4,931,199, and 5,093,432, and using the suitable starting materials with the proper end groups, compositions described in the patent can be prepared.

The hydrocarbon polyether can be combined with a solvent such as FREON®
30 113 to produce a fluorination mixture, optionally in the presence of a hydrogen fluoride scavenger such as potassium fluoride. A fluid mixture containing fluorine

and an inert diluent such as nitrogen can be introduced to the fluorination mixture for a sufficient period of time to convert substantially or essentially all hydrogen atoms to fluorine atoms. The flow rate of the fluid can be in the range of from about 1 to about 25000 ml/min, depending on the size of the fluorination mixture.

- 5 The fluoropolyether can also be introduced after the introduction of the fluorine-containing fluid at a rate such that a perfluorination of the prepolyether can be accomplished.



$C_rF_{(2r+1)}O-(CF(CF_3)CF_2-O)_wC_rF_{(2r+1)}$, where r is 3 to 6 and w is 4 to 100;

- 10 $C_rH_{(2r+1)}O-(C_2H_4-O)_wC_rH_{(2r+1)} \rightarrow$

$C_rF_{(2r+1)}O-(C_2F_4-O)_wC_rF_{(2r+1)}$, where r is 3 to 6 and w is 4 to 100;



$C_rF_{(2r+1)}O-(C_2F_4-O)_w(C_3F_6-O)_wC_rF_{(2r+1)}$, where r is 3 to 6, and each w is independently 4 to 100;

- 15 $C_rH_{(2r+1)}O-(CH_2CH_2CH_2-O)_w(CH(CH_3)CH_2-O)_uC_rH_{(2r+1)} \rightarrow$

$C_rF_{(2r+1)}O-(CF_2CF_2CF_2-O)_w(CF(CF_3)CF_2-O)_uC_rF_{(2r+1)}$, where r is 3 to 6, w is 4 to 100, and u is 0 to 100.

While the procedures for replacing end groups with C₃ - C₆ end groups can also be practiced on the FOMBLIN® fluids described above, the value of inserting

- 20 the more stable end groups is severely limited due to the presence of the chain destabilizing -O-CF₂-O- segments therein.

The PFPE fluids of the invention can be purified by contact with absorbing agents, such as charcoal or alumina, to remove polar materials and fractionated conventionally by distillation under reduced pressure by any method known to one skilled in the art.

According to the fourth embodiment of the invention, a thermal stable grease or lubricant composition is provided. Greases containing the perfluoropolyether disclosed in the first embodiment of the invention can be produced by combining the perfluoropolyether with a thickener. Examples of such thickeners include, but are not limited to, standard thickeners such as, for example,

poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof. The thickeners can be present in any appropriate particle and sizes as known to one skilled in the art.

According to the invention, the perfluoropolyether of the invention can be
5 present in the composition in the range of from about 0.1 to about 50, preferably 0.2 to 40, percent by weight. The composition can be produced by any methods known to one skilled in the art such as, for example, by blending the perfluoropolyether with the thickener.

EXAMPLES

10 Example 1 and Comparative Examples A and B.

Separation of $F[CF(CF_3)CF_2O]_6CF(CF_3)_2$ (IPA-F, Example 1), $F[CF(CF_3)-CF_2-O]_6-CF_2CF_3$ (EF, Comparative Example A) and $F[CF(CF_3)-CF_2-O]_7-CF_2CF_3$ (EF, Comparative Example B) from KRYTOX® Fluid ($F[CF(CF_3)-CF_2-O]_n-R_f$, n = 3-11) by Fractional Distillation.

15 Samples for the aforementioned Examples were obtained via successive fractional vacuum distillations of KRYTOX® Heat Transfer Fluids. In the first distillation, a 100-cm long, 3-cm ID (inner diameter) column was used. The column was packed with Raschig rings made from 1/4" OD (outer diameter)/3/16" ID FEP (fluorinated ethylene polypropylene) tubing (obtained from Aldrich, Milwaukee, Wisconsin) cut into pieces about 1/4" long. The distillation was carried out under dynamic vacuum conditions, and a pure sample of $F[CF(CF_3)-CF_2-O]_7-CF_2CF_3$ (Comparative Example B) where n = 7 (approximately 350 g) was obtained at an overhead temperature of 88 - 92°C as a fraction. At this point, previous fractions were combined and fluorinated with elemental fluorine at 100°C in the presence of
20 NaF in order totally to remove all $F[CF(CF_3)-CF_2-O]_n-CHFCF_3$ prior to the second distillation.
25

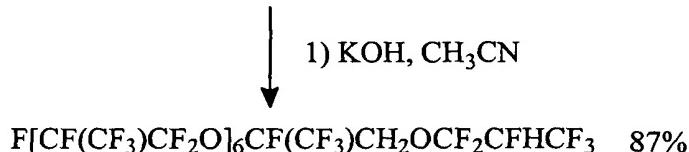
For the second distillation, a 120-cm long, 2.4-cm ID column packed with 1/4" Monel saddle-shaped packing was used. This distillation was again carried out under dynamic vacuum (about 20 mTorr, 2.7 kPa), and pure samples of $F[CF(CF_3)-CF_2-O]_6-CF_2CF_3$ (Comparative Example A) with an overhead temperature of 68 -
30

72°C (200 g) and F[CF(CF₃)-CF₂-O]₆-CF(CF₃)₂ (Example 1) with an overhead temperature of 72 - 73°C (85 g) were collected.

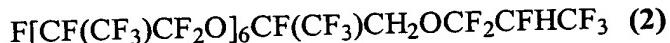
Example 2.

This example illustrates the production of a perfluoropolyether having paired
5 perfluoro-n-propyl end groups.

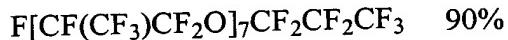
Addition of Hexafluoropropene (HFP) to a perfluoropolyether Alcohol



A perfluoropolyether alcohol (KRYTOX® alcohol, available from E.I. du Pont de Nemours & Company, Wilmington, Delaware; 100.00 g, 87.2 mmol, 1146g/mol)
10 was added to a 250-ml round-bottomed flask. Acetonitrile (160 ml, 12.4 g, 0.302 mol) and finely ground potassium hydroxide (4.87 g, 86.8 mmol) was then added to the flask with a magnetic stir bar to make a reaction mixture. Once the flask was connected to a vacuum line, the mixture was degassed. Upon vigorous stirring, the reaction mixture was heated to 60°C. When the temperature reached 60°C, a constant pressure of 650 mmHg (87 kPa) of hexafluoropropene was applied to the same flask.
15 Stirring and applied pressure was maintained until the reaction did not take up any more hexafluoropropene. A color change was observed during the reaction from a light yellow to a dark orange when the reaction was completed. After the reaction, water was added to the reaction mixture and the bottom layer was removed via a separatory funnel. This was done three times to insure a clean product. Lastly, any solvent in the fluorous product later was stripped by vacuum. Final mass of product,
20 a perfluoropolyether-alcohol HFP adduct, was 97.77 g (86.5% yield).

Fluorination of perfluoropolyether-alcohol HFP Adduct

↓
20% F₂/ 80% N₂



FREON® 113 (500 ml) and potassium fluoride (13.13 g, 22.6 mmol) were added to a fluorination reactor. Upon addition, the reactor was quickly closed and purged with dry nitrogen for 30 min at a rate of 300 ml/min. Next, the reactor was purged with 20%fluorine/ 80 % nitrogen for 30 min at a flow of 250 ml/min. The perfluoropolyether-alcohol HFP adduct (97.77g, 7.54 mmol, 1.88 g/ml, 1296 g/mol) was then added to the reactor via a pump at a rate of 0.68 ml/min with 480-490 ml/min flow of 20% fluorine, at a reactor stir rate of 800 rpm and a temperature of 25-28°C for 76 min. In the next 30 min, the pump line was washed with an additional 20 ml of FREON® 113. After a 106 min run time, the flow of fluorine was reduced to 250 ml/min for the next 60 min and then 40 ml/min with a stir rate of 600 rpm for the next 2 days. After the reaction, the system was purged with nitrogen. The product was removed and washed with water. The bottom layer was removed with a separatory funnel and the FREON® was stripped from the product via the vacuum line. Final mass of the product was 91.96 (90.3% yield).

TEST METHOD AND RESULTSTest Method. Procedure for Measuring Thermal Stability

A 75-ml stainless steel Hoke® cylinder topped with a 10-cm stainless steel spacer and valve was used to contain the poly(HFPO) sample for each thermal stressing experiment. The mass of the cylinder was taken and recorded after every step in the procedure. In a dry box, the cylinder was charged with AlF₃ (ca. 0.05 g), weighed, and then charged with a sample of monodisperse poly(HFPO) which contained predominately perfluoroisopropyl end-groups (ca. 1.65 g, purity > 99%). (The AlF₃ used in these experiments was synthesized by the direct fluorination of AlCl₃ and was shown by X-ray powder diffraction to largely be amorphous.) The

cylinder was then removed from the dry box and placed in a thermostatic oil bath at a predetermined temperature in the range of $190\text{--}230 \pm 1.0^\circ\text{C}$. The valve was kept cool by diverting a stream of room-temperature compressed air over it. After a period of 24 hours, the cylinder was cooled to room temperature, weighed, and then 5 cooled further to liquid nitrogen temperature (-196°C). Any non-condensable materials were stripped from the cylinder under dynamic vacuum. The cylinder was then warmed to room temperature, and the volatile materials were removed by vacuum transfer and stored for later analysis by FT-IR and NMR spectroscopy. Methanol was then added to the cylinder to convert any acid fluorides that might 10 have resulted from the degradation to their corresponding methyl esters. The resulting non-volatile material was then separated from any unreacted methanol and analyzed and analyzed by GC-mass spectrometry. The results from this experiment as well as those from additional and related experiments where the monodisperse 15 poly(HFPO) samples have either perfluoroisopropyl, perfluoroethyl, perfluoro-n-propyl, or perfluoro-t-butyl end-groups are shown in Table 1.

Table 1

Temperature ($^\circ\text{C}$)	200	210	220	230	240	260	270
Comparative Example A and B							
Percent of $\text{F}[\text{HFPO}]_6\text{-CF}_2\text{CF}_3$ (Comparative Example A) degraded	--	37.4	96.3	--	--	--	--
Percent of $\text{F}[\text{HFPO}]_7\text{-CF}_2\text{CF}_3$ (Comparative Example B) degraded	1.8	30.8	--	--	--	--	--
Percent of $\text{F}[\text{HFPO}]_6\text{-CF}(\text{CF}_3)_2$ (Example 1) degraded	--	6.2	14.2	12.6	11.7	51.9	86.2
Percent of $\text{F}[\text{HFPO}]_7\text{-CF}_2\text{CF}_2\text{CF}_3$ (Example 2) degraded	--	--	0	--	--	81.8	--

Table 1 shows a substantial reduction in the amount of degradation of a poly(HFPO) fluid having either paired perfluoro-i-propyl end groups or a 20 poly(HFPO) fluid having paired perfluoroethyl and perfluoro-i-propyl end groups when heated with AlF_3 , as compared with the poly(HFPO) fluid having a terminal n-

propyl and ethyl end, demonstrating the greater stabilizing effect of the perfluoro-propyl terminal groups.